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DESCRIPTION

Nb-Al ALLOY POWDER FOR ELECTROLYTIC CAPACITORS, METHOD FOR
MANUFACTURING Nb-Al ALLOY POWDER, AND ELECTROLYTIC CAPACITOR

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Technical Field

The present invention relates to an Nb-Al alloy powder
for electrolytic capacitors and an electrolytic capacitor
manufactured using such a powder.

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Background Art

In recent years, in order to manufacture electronic
devices, capacitors having the following advantages have
been demanded: small size, high capacitance, reasonable
15 price, and stable supply. To such capacitors are usually
prepared anodes including sintered bodies made from a
tantalum powder because the capacitors of tantalum powder
are relatively compact and have a high capacitance and
superb performance as capacitor. However, the tantalum
20 capacitors are highly expensive and users are unsure about
the stable supply thereof. In particular, an increase in
capacitance leads to an increase in the amount of tantalum
contained in the capacitors. Therefore, a new material,
other than tantalum, for capacitor electrodes has been
25 recently demanded.

ATTACHMENT A

In order to achieve compact high-capacitance electrolytic capacitors containing a metal material other than tantalum, numerous attempts have been made to develop capacitor anodes containing niobium (Japanese Unexamined Patent Application Publication No. 55-157226 or other documents). This is because niobium oxide has a higher dielectric constant than that of tantalum oxide and niobium is inexpensive and readily available. Japanese Unexamined Patent Application Publication Nos. 60-66806, 60-216530, and 1-124212 disclose anodes made from a niobium-aluminum alloy powder or anodes including sheets of niobium-aluminum alloy foil. An electrolytic capacitor including an anode made from a niobium powder as disclosed in any one of the above documents has problems in that dielectric layers containing niobium oxide are thermally unstable and this capacitor reflow-soldered has inferior leakage current properties as compared to the tantalum capacitors. The anodes made of the niobium-aluminum alloy as disclosed in Japanese Unexamined Patent Application Publication No. 60-66806 and the like have a problem in that oxide films derived from the niobium-aluminum alloy have an insufficient dielectric constant although the films have high thermal stability. This is because the niobium content of the alloy is insufficient. Since the alloy sheets are produced by a rapid quenching process and then directly processed into the anodes, the

anodes further have a problem in that the anodes are inferior in specific surface area as compared to those made from a tantalum powder or a niobium powder; hence, the anodes are unsuitable for high-capacitance capacitors. That is, the anodes are unsuitable for practical use.

The present invention has been made to solve the above problems. It is an object of the present invention to provide an Nb-Al alloy powder for manufacturing electrolytic capacitors which include stable dielectric layers and which have a high capacitance and breaking voltage.

When the Nb-Al alloy powder has an increased Nb content and further contains a single third element or a plurality of third elements in addition to Nb and Al, electrolytic capacitors which include dielectric layers containing an oxide with a high dielectric constant and which have a high capacitance and breaking voltage can be manufactured using the powder.

Furthermore, it is another object of the present invention to provide an electrolytic capacitor manufactured using the Nb-Al alloy powder.

Disclosure of Invention

In order to achieve the above objects, the present invention provides a powder, capacitor, and method described below.

A Nb-Al alloy powder for electrolytic capacitors according to the present invention includes particles having dendritic microstructures and matrices. The dendritic microstructures principally contain NbAl_3 , Nb_2Al , Nb_3Al , or
5 Nb. The matrices contain eutectic structures or Al. The eutectic structures contain at least two selected from the group consisting of NbAl_3 , Nb_2Al , Nb_3Al , and Nb. The matrices surround the dendritic microstructures. The particles that are processed to be used electrolytic
10 capacitor anode are covered with dielectric layers when the powder is processed into an anode of an electrolytic capacitor.

If the particles are processed so as to have a fine size, the Nb-Al alloy powder is useful in manufacturing
15 capacitors having a higher breaking voltage and capacitance than those of capacitors including anodes prepared by sintering a powder including primary tantalum particles.

The dielectric layers of the Nb-Al alloy powder contain niobium oxide and aluminum oxide; hence, the dielectric
20 layers have a high dielectric constant and low leakage current and are more stable than those containing niobium oxide only.

The Nb-Al alloy powder has an advantage in that the particles can be readily rendered porous by partly or
25 entirely removing the matrices to allow the dendritic

microstructures to occupy the most part of the surface of the particles. If a capacitor anode is made from the porous particles by removing the matrices as described above, the anode has a large surface area and includes dielectric layers having a high breaking voltage; hence, an electrolytic capacitor composed of such anode exhibits high performance.

In the Nb-Al alloy powder, the Nb-Al alloy may have an aluminum content of 46% to 90% on a mass basis, the dendritic microstructures principally contain NbAl_3 , and the matrices contain Al. The matrices surround the dendritic microstructures. The surface area of the Nb-Al alloy powder can be increased, because the matrices can be readily removed by an etching process.

In the Nb-Al alloy powder, the Nb-Al alloy has an aluminum content of 27% and more and less than 46% on a mass basis, the dendritic microstructures principally contain NbAl_3 , and the eutectic matrices contain NbAl_3 and Nb_2Al . The matrices surround the dendritic microstructures.

In the Nb-Al alloy powder, the Nb-Al alloy may have an aluminum content of 14% and more and less than 27% on a mass basis, the dendritic microstructures principally contain Nb_2Al , and the eutectic matrices contain NbAl_3 and Nb_2Al . The matrices surround the dendritic microstructures.

In the Nb-Al alloy powder, the Nb-Al alloy may have an

aluminum content of 10% and more and less than 14% on a mass basis, the dendritic microstructures principally contain Nb_3Al , and the matrices contain eutectic microstructure containing Nb_3Al and Nb_2Al . The matrices surround the
5 dendritic microstructures.

In the Nb-Al alloy powder, the Nb-Al alloy may have an aluminum content of less than 10% on a mass basis, the dendritic microstructures principally contain Nb, and the eutectic matrices contain Nb_3Al and Nb. The matrices
10 surround the dendritic microstructures.

In the Nb-Al alloy powder, the Nb-Al alloy may contain at least one element selected from the group consisting of tantalum, titanium, hafnium, zirconium, molybdenum, barium, strontium, and boron. When the Nb-Al alloy contains at
15 least one of those elements, the dielectric layers formed on the particle surfaces, hence such electrolytic capacitor as prepared by processing the powder have an extremely high dielectric constant.

In the Nb-Al alloy powder, the element content is
20 preferably 3% and less on a mass basis. When the element content is more than 3% on a mass basis, oxide films present on an anode made from the powder have unstable dielectric properties and this causes an increase in leakage current under high breaking voltage conditions; that is,
25 disadvantages arise.

In the Nb-Al alloy powder, the Nb-Al alloy preferably contains 100 ppm and less of an iron impurity. When the iron impurity content is more than 100 ppm, the dielectric layers have a low breaking voltage. This is not preferable.

5 In the Nb-Al alloy powder, the dendritic microstructures preferably have a dendrite arm spacing (width) of 3 μm and less. According to such a configuration, the surface of the particles can be increased, whereby high-capacitance electrolytic capacitors can be manufactured
10 using the particles. In particular, if the particles are rendered porous by removing the matrices by an etching process, the resulting particles have a particularly large surface area.

In the Nb-Al alloy powder, the particles preferably
15 have a bulk density of 2.8 to 5.0 g/cm^3 .

In the Nb-Al alloy powder, the particles preferably have a specific surface area of 1 to 10 m^2/g .

An electrolytic capacitor according to the present invention includes an anode prepared by sintering the powder
20 described above. The electrolytic capacitor having such a configuration is compact and has a high capacitance.

A method for manufacturing an Nb-Al alloy powder includes a step of quenching a molten Nb-Al alloy having an aluminum content of 27% to 90% on a mass basis to form
25 particles or thin sheets, both having dendritic

microstructures with dendrite arm spacing of 3 μm and less. The powder includes particles, which are covered with dielectric layers when the powder is processed into an anode of an electrolytic capacitor.

5 According to the above method, the surface area of the particles can be readily increased by etching the particles because matrices or dendritic phase regions present in the particles are preferentially etched off and the dendritic microstructures are allowed to remain in the particles,
10 which are thereby rendered porous. In the Nb-Al alloy powder, the particles are fine and have a large surface area. If dielectric layers containing an oxide are formed on the particles, the dielectric layers have a high dielectric constant. Therefore, compact electrolytic capacitors having
15 a high capacitance can be manufactured using the powder.

 In the method, the molten Nb-Al alloy is preferably quenched at a rate of 10^3 °C/sec and higher. When the quenching rate is such a value, the dendritic microstructures can be efficiently formed in the particles
20 or the thin sheets. Therefore, the particles obtained from the particles (rapidly quenched powder) or the thin sheets have a large surface area. The quenching rate is more preferably 10^4 °C/sec and more.

 The method may further include a step of pulverizing
25 the rapidly quenched powder or the thin sheets.

Best Mode for Carrying Out the Invention

The Nb-Al alloy powder for electrolytic capacitors according to the present invention as described above is characterized in that this powder includes particles which have dendritic microstructures principally containing Nb and/or Nb-Al intermetallic compound and which have matrices containing another Nb-Al intermetallic phase. The dendritic microstructures have branched extensions and the matrices surround the dendritic microstructures. Since the particles have such crystal structures, the size of the particles can be greatly reduced readily. That is, the particle size of this powder is much less than the size of primary particles included in a tantalum powder for manufacturing known electrolytic capacitors. A sintered body made of the Nb-Al alloy powder therefore has a large surface area. If the Nb-Al alloy powder is used to manufacture electrolytic capacitors, dielectric layers which cover the large surface area with high dielectric constant can be formed on the particles. Therefore, the electrolytic capacitors obtained are compact and have a high capacitance.

In the powder of the present invention, whose dendritic phase is principally $NbAl_3$ dendritic microstructures, and whose matrices contain Nb_2Al or Al , the dielectric layer formed on the particles contains niobium oxide and aluminum

oxide. The matrices surround the dendritic microstructures. When an anode of an electrolytic capacitor is made from this powder, the capacitor has a higher dielectric constant than that of an aluminum capacitor. Also the dielectric layers
5 are greatly superior in stability as compared to those containing niobium oxide only. If this powder is used to manufacture electrolytic capacitors, the electrolytic capacitors obtained are compact and have a high capacitance.

Nb is more inexpensive as compared to Ta usually used
10 to manufacture current electrolytic capacitors. Therefore, the Nb-Al alloy powder has an advantage in that a type of electrolytic capacitor having substantially the same performance as that of Ta capacitors can be manufactured at low cost.

15 An example of a method for manufacturing the Nb-Al alloy powder according to the present invention will now be described.

(1) In order to manufacture the Nb-Al alloy powder, a molten alloy having a predetermined Nb content and Al
20 content is prepared. In this method, the composition of the alloy may be arbitrarily varied.

(2) The molten alloy is rapidly quenched and thereby formed into powders by a gas atomizing process or an RSR process (rotating electrode process) or formed into a thin
25 sheet by a melt-spinning process. The powders or the sheets

are then pulverized with a ball mill or a jet mill, whereby the Nb-Al alloy powder is obtained. If the powders or the sheets prepared in the rapid quenching step are hydrogenated in a hydrogenation step and then pulverized, a finer alloy powder can be obtained.

In the method of the present invention, if any one of the above processes is used, manufacturing conditions are preferably set such that the quenching rate is 10^3 °C/sec and higher, and more preferably 10^4 °C/sec and higher. When the quenching rate is as described above, the dendritic microstructures can be efficiently formed in the particles or the sheets. This allows the particles to have a large surface area.

According to the above procedure, the Nb-Al alloy powder of the present invention can be manufactured. This powder includes particles which have dendritic microstructures principally containing intermetallic compound and which have matrices containing another intermetallic compound and the matrices surround the dendritic microstructures.

When the Nb-Al alloy powder has an aluminum content of 27% and more on a mass basis, the surface of the particles can be increased by etching the particles; hence, high-capacitance capacitors can be manufactured using the resulting particles. In particular, the matrices

surrounding the dendritic microstructures principally containing NbAl_3 are partly or entirely removed by an etching process, whereby the dendritic microstructures acting as skeletal structures are allowed to remain and the particles are therefore rendered porous.

When the matrices of the particles contain, for example, Al, the matrices can be readily etched off; that is, the matrices can be selectively removed with an ordinary etching solution containing hydrochloric acid or nitric acid, whereby the particles are rendered porous. When the particles have eutectic structures containing NbAl_3 and Nb_2Al in addition to the dendritic microstructures principally containing NbAl_3 , the surface area of the particles can be increased by etching off portions containing NbAl_3 with hydrofluoric acid or nitric acid; hence, the powder is useful in manufacturing high-capacitance capacitors.

[EXAMPLES]

Examples of the present invention will now be described.

Table 1 shows Nb-Al alloy powders, prepared in Example 1, including particles having an Al content of 20% to 75% on a mass basis. The powders referred to as Samples 3 and 6 included particles having an Al content of 46% to 90% on a mass basis and the particles had mixed structure of Al matrices and NbAl_3 dendritic microstructures as primary

crystal; hence, the surface area of the particles were greatly increased by etching the particles with an etching solution containing hydrochloric acid or nitric acid. The etched particles were processed into sintered bodies, which
5 were subjected to anordizing, whereby the following elements were obtained: elements having a CV value and breaking voltage greater than those of elements made from a tantalum powder.

[Table 1]

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV/g}$	Leakage Current μA
1	Nb and 20% Al	Quenching*1 and then pulverization	1.2	4.5	40	80,000	Less than 0.3
2	Nb and 40% Al	Quenching*1 and then pulverization	1.5	4.2	100	43,000	Less than 0.3
3	Nb and 75% Al	Quenching*1 and then pulverization	1.5	3.9	240	16,000	Less than 0.5
4	Nb, 20% Al, and 3% Zr	Quenching*1 and then pulverization	1.4	4.4	120	33,000	Less than 0.5
5	Nb, 40% Al, and 5% Zr	Quenching*1 and then pulverization	1.3	4.2	240	14,000	Less than 0.5
6	Nb, 75% Al, and 5% Zr	Quenching*1 and then pulverization	1.8	3.7	480	20,000	Less than 0.5

(*1) Quenching by a melt spinning process using a single roll

Table 2 shows powders, prepared in Example 2, including particles having an Al content of 27% and more and less than 46% on a mass basis. The powders having the above content were prepared by atomization under rapid solidification conditions and the particles had mixed structure of NbAl_3 - Nb_2Al eutectic structures and NbAl_3 dendritic microstructures as primary crystal. Portions containing NbAl_3 were etched off with a solution containing hydrofluoric acid and nitric acid, whereby the surface area of the particles was greatly increased. The resulting particles were processed into sintered bodies, which were subjected to anodizing, whereby the following elements were obtained: elements having a CV value and breaking voltage greater than those of elements made from a tantalum powder.

[Table 2]

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV}/\text{g}$	Leakage Current μA
1	Nb and 35% Al	Quenching by a gas atomizing process and then etching	35	3.5	120	16,000	Less than 0.5
2	Nb, 10% Ta, and 35% Al	Quenching by an RSR process	1.5	3.8	120	33,000	Less than 0.5
3	Nb, 3% Zr, and 35% Al	Quenching by an REP process, pulverization, and then etching	1.5	3.2	120	28,000	Less than 0.5
4	Nb and 35% Al	Quenching by a gas atomizing process and then etching	55	3.4	240	13,000	Less than 0.5

[Table 2] (Continued)

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage V_f	CV Value $\mu\text{FV}/\text{g}$	Leakage Current μA
5	Nb, 10% Ta, and 35% Al	Quenching by a gas atomizing process and then etching	50	3.9	240	12,000	Less than 0.5
6	Nb, 3% Zr, and 35% Al	Quenching by an REP process, pulverization, and then etching	1.2	3.6	240	25,000	Less than 0.5
7	Nb, 10% Ta, and 30% Al	Quenching by an REP process	1.3	3.2	240	32,000	Less than 0.5

[Table 2] (Continued)

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV/g}$	Leakage Current μA
8	Nb, 10% Ta, 30% Al, and 5% Ba	Quenching by an REP process, pulverization, and then etching	1.3	3.9	480	20,000	Less than 0.1
9	Nb, 10% Ta, 30% Al, and 3% Sr	Quenching by an REP process, pulverization, and then etching	1.2	3.9	400	16,000	Less than 0.1

Table 3 shows powders, prepared in Example 3, including particles having an Al content of 14% and more and less than 27% on a mass basis. The powders having the above content were prepared by atomization under rapid solidification conditions and the particles had mixed structure of NbAl_3 - Nb_2Al eutectic structures and Nb_2Al dendritic microstructures as primary crystal. The Nb_2Al dendritic microstructures were etched off with a solution containing hydrofluoric acid and nitric acid, whereby the surface area of the particles was greatly increased. The resulting particles were processed into sintered bodies, which were subjected to anordizing, whereby the following elements were obtained: elements having a CV value and breaking voltage greater than those of elements made from a tantalum powder.

[Table 3]

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV}/\text{g}$	Leakage Current μA
1	Nb and 20% Al	Quenching by an REP process, pulverization, and then etching	1.2	3.6	120	35,000	Less than 0.5
2	Nb and 20% Al	Quenching by a gas atomizing process, pulverization, and then etching	1.7	3.8	120	47,000	Less than 0.5
3	Nb and 20% Al	Quenching by an RSR process, pulverization, and then etching	1.5	3.7	120	38,000	Less than 0.5

[Table 3] (Continued)

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage V_f	CV Value $\mu\text{FV}/\text{g}$	Leakage Current μA
4	Nb and 20% Al	Quenching by a gas atomizing process, pulverization, and then etching	5.5	3.1	120	22,000	Less than 0.5
5	Nb, 20% Al, and 5% Ba	Quenching by an REP process, pulverization, and then etching	1.2	3.6	240	40,000	Less than 0.5

Table 4 shows powders, prepared in Example 4, including particles having an Al content of 10% and more and less than 14% on a mass basis. The powders having the above content were prepared by atomization under rapid solidification conditions and the particles had mixed structure of Nb₃Al-Nb₂Al eutectic structures and Nb₃Al dendritic microstructures as primary crystal. The particles were allowed to absorb hydrogen and then pulverized into fine particles, which were processed into sintered elements having a significantly large surface area. The sintered elements were subjected to anodizing. The resulting sintered elements had a CV value and breaking voltage greater than those of elements made from a tantalum powder.

[Table 4]

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV}/\text{g}$	Leakage Current μA
1	Nb and 12% Al	Quenching by an RSR process, pulverization, and then etching	1.3	3.6	24	145,000	Less than 0.5
2	Nb and 12% Al	Quenching by a gas atomizing process, pulverization, and then etching	1.6	3.8	80	51,000	Less than 0.5
3	Nb and 12% Al	Quenching by an RSR process, pulverization, and then etching	1.6	3.7	120	29,000	Less than 0.5

[Table 4] (Continued)

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage V_f	CV Value $\mu\text{FV/g}$	Leakage Current μA
4	Nb, 5% Ta, and 12% Al	Quenching by a gas atomizing process, pulverization, and then etching	5.2	3.1	120	35,000	Less than 0.5
5	Nb, 12% Al, and 5% Ba	Quenching by an RSR process, pulverization, and then etching	1.1	3.6	240	24,000	Less than 0.5

Table 5 shows powders, prepared in Example 5, including particles having an Al content of less than 10% on a mass basis. The powders having the above content were prepared by atomization under rapid solidification conditions and the particles had mixed structure of Nb₃Al-Nb eutectic structures and Nb dendritic microstructures as primary crystal. The particles were allowed to adsorb hydrogen and then pulverized into fine particles, which were processed into sintered elements having a significantly large surface area. The sintered elements were subjected to anodizing. The resulting sintered elements had a CV value and breaking voltage greater than those of elements made from a tantalum powder.

[Table 5]

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV/g}$	Leakage Current μA
1	Nb and 7% Al	Quenching by an RSR process, pulverization, and then etching	1.1	3.6	80	75,000	Less than 0.5
2	Nb and 7% Al	Quenching by a gas atomizing process, pulverization, and then etching	1.4	3.8	80	65,000	Less than 0.5
3	Nb and 7% Al	Quenching by an RSR process, pulverization, and then etching	1.5	3.7	120	30,000	Less than 0.5

[Table 5] (Continued)

Samples	Composition	Procedures for Preparing Powders	Particle size d_{50} μm	Bulk Density of Sintered Elements gr/cm^3	Formation Voltage Vf	CV Value $\mu\text{FV}/\text{g}$	Leakage Current μA
4	Nb, 5% Ta, and 7% Al	Quenching by a gas atomizing process, pulverization, and then etching	2.2	4.1	120	32,000	Less than 0.5
5	Nb, 7% Al, and 5% Ba	Quenching by an RSR process, pulverization, and then etching	1.1	3.6	240	25,000	Less than 0.5

Industrial Applicability

As described above in detail, the Nb-Al alloy powder according to the present invention includes the particles, which are covered with the dielectric layers when the powder is processed into an anode of an electrolytic capacitor. The particles have the dendritic microstructures principally containing NbAl_3 , Nb_2Al , Nb_3Al , or Nb and the matrices containing Al or the eutectic structures containing two selected from the group consisting of NbAl_3 , Nb_2Al , Nb_3Al , and Nb. The matrices surround the dendritic microstructures. The particles therefore are extremely fine. Since the dielectric layers on the particles contain niobium oxide and aluminum oxide, the dielectric layers have a high dielectric constant and low leakage current and are superior in stability as compared to those containing niobium oxide only. Therefore, the powder is extremely useful in manufacturing a sintered body, having a breaking voltage greater than that of a known tantalum sintered body, for manufacturing a high-capacitance electrolytic capacitor.

If the matrices are partly removed by etching the particles, the resulting particles are porous and have a greatly increased surface area because the dendritic microstructures acting as skeletal structures remain. This leads to an increase in the capacitance of electrolytic capacitors.